50X1-HUM

Next 1 Page(s) In Document Denied

Titrimetric Determination of Zirconium in
Zirconium Silicate or in Metallic Aggregates

1. Standard Method

a. Preparation

0.5 grams of the silicate are fused with 10 g of sodium carbonate for 30 minutes. The mass is attacked with IN HNO_3 first diluted (75 ml) then concentrated (40 ml) by boiling for 15 minutes. Silica precipitates and after diluting the system with 150 ml of water solids are filtered and washed till neutral with warm water. After cooling the mother liquor is treated with NH_4OH to precipitate $Zr(OH)_4$.

The hydroxide is filtered off, washed till neutral and dissolved with HNO_3 (70 ml N/6) under heating. The filter is washed and the liquid cooled to room temperature and brought to 1000 ml.

b. Titration

To 20 ml are added four drops of a 0.04% bromcresol purple and the system is neutralized with concentrated KOH and then with N/10 KOH or HNO_3 if necessary. To the neutral solution is added a mixture of 20 ml of N/10 HNO_3 and 1.35 ml of freshly prepared IN KF and the system is left at rest for five minutes.

(The KF solution should be added to HNO_3.) After adding further three drops of the indicator, excess of acid is titrated with N/10 KOH.

Consequently: 2.2805 x ml of N/10 HNO_3 = mg Zr

or 3.0805 x ml of N/10 HNO_3 = mg ZrO_2

(Each cc of the KF solution requires 0.092 cc of N/10 HNO_3.)

To adopt this method to metallic zirconium the following modification is in order:

100 mg of filings are dissolved in 10 ml of concentrated H_2SO_4 and diluted with 50 ml of water. Zirconium hydroxide is precipitated with ammonia at pH 10 to 11.

2. Accelerated Method

Since the above method requires considerable time for filtration of silica it was established that titration of zirconia is possible even in presence of silica, provided that the back-and-forth method of acidulation and alkalinization is performed two to three times. Presumably under these conditions stepwise reactions of the indicator are eliminated which otherwise occur in the presence of silica. These stepwise reactions are shown through strong yellow coloration of the bromcresol purple in acid solution passing through a range of reds to final blue.

Specifically, this method eliminates precipitation and filtration of zirconium hydroxide as well as careful elimination of silica. Portions of the liquid are

grossly separated from silica by means of a large pleated paper filter and titrated in presence of the indicator as shown above.

Tests indicated errors of the order of $\pm$ 0.2% (average value of six tests $\pm$ 0.16%).

The reactions involved may be shown as follows:

$$Zr(OH)_4 + 6\ KF + 4\ HNO_3 \longrightarrow K_2\ ZrF_6 + 4\ KNO_3 + 4\ H_2O$$

$$3\ KF + 2\ HNO_3 \longrightarrow HF + 2\ KNO_3 + KHF_2$$